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PERSPECTIVES

Unique features of the nano-scale

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Abstract Ten features that uniquely arise at the nano size range are discussed. These include those based on the obvious—the physically small size and concomitant large surface to volume ratio features. Importantly, they also include more subtle features that emerge at this scale including self-assembly possibilities, quantum confinement and tunneling, wave-particle duality, and plasmonic behavior. In addition, the list of ten encompasses very curious features that can manifest themselves at the nano-scale. These include enhanced friction and striction due to the Casimir "force" coming from quantum fluctuations as well as zero mass Dirac electrons which can arise from relativistic effects. The presence of Dirac electrons can result in very unusual material properties including ballistic charge transport, unusual Hall effects, enormously high carrier mobilities, and topologically dependent phases. The latter includes topological insulators, nano-materials characterized by having carriers with spin-momentum locking. A second type of nano-scale fluctuation behavior is also on the list of ten unique features of the nano size range: thermal fluctuations. These result in the statistical fluctuations around an average distribution becoming more observable thereby blurring the second law of thermodynamics at the nano-scale.

Keywords Thermal fluctuations · Quantum fluctuations · Quantum confinement · Relativity · Dirac electrons · Self-assembly

Introduction

Nanotechnology is the practice of engineering, medicine, and science at the nano-scale—the size range of things as diverse as viruses, topological insulators, ribosomes, relativistic Dirac electrons, and superparamagnetic nanoparticles. It is a size range that offers unique attributes, new vistas, and new opportunities.

The uniqueness of the nano-scale has been previously discussed in the literature, often using phenomenological approaches that focus on the impact of nano-scale material properties on a specific application. An example is found in a 2013 article on drug delivery applications (Otto and de Villiers 2013) which deals with heat transfer, crystallization, glass transition temperature, melting point, dissolution, and solubility in drug-relatednano-scale materials. There is a second approach to addressing the uniqueness of the nano-scale. This approach brings attention to the basic, universally applicable scientific features that emerge in the nano-range. Size is obviously one of these basic features but so are quantum effects such as quantum fluctuations which cause nano-scale

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striction and friction, basic relativity effects which can result in the relativistic Dirac electron behavior in some 2D nano-materials and topological insulators, and thermal fluctuations which can lead to a breakdown of the second law of thermodynamics. This all-encompassing second approach, which we follow in this article, is exemplified by a recently published 2018 text (Fonash and Van de Voorde 2018). Following this text, we come to the conclusion that the uniqueness of the nano-scale is due to ten basic features of this size range. This second approach, focusing on the basics, seems the obvious path to follow for this special issue "Unifying Concepts for Nanoscience and Nanosystems."

Unique features of the nano-scale

We initiate an overview of our tabulation of the unique features of the nano-scale by first considering the obvious feature—the physical size of nanoparticles and nanograins. This physical size is compatible with many structures in the world of biology such as the pores in cell walls, the diameter of DNA, and nature's ubiquitous nanoparticle—the virus (Fonash and Van de Voorde 2018). Further, physical size dictates surface to volume ratio and consequently the relative importance of surface forces versus bulk forces and of surface atom properties versus bulk atom properties. Importantly, morphology and not just the size of nanostructures uniquely affect chemical bonding and self-assembly possibilities. In addition, the minute size range of the nano-scale also gives rise to the emergence of quantum confinement, wave-particle duality behavior, and relativistic effects such as Dirac electrons. The final features on this list of ten basic aspects of the nano-scale are unique electromagnetic (E-M) interactions that can be present with nano-materials (e.g., plasmonics) and the possible presence of scale-caused fluctuations including quantum fluctuations and thermal fluctuations.

Smallness: physical size

We now begin looking in more detail at the repercussions of the ten unique features of the nano-scale. For example, the physical smallness of nanoparticles and their compatibility with the basic structures of biology can be exploited to make them potentially excellent delivery vehicles for medical applications, as seen in the example of Fig. 1. Also, their surface chemistry can be adjusted to allow functionalization, i.e., the attachment of molecules to allow their collection in the plaque structure seen on the artery wall. These targeted delivery vehicles can be engineered to carry cargoes for immunotherapy as well as for drug therapy treatments. They can also carry fluorescent agents to improve imaging and to monitor treatment efficacy (Gadde and Rayner 2016).

Smallness: surface versus bulk forces

The unique feature of the large to surface to volume ratio of nanograins and nanoparticles is that for small enough grains and particles, the forces acting in or on the surfaces can become very important relative to forces acting in the bulk. This applies to nanostructure atom to atom forces. It also applies to forces arising from outside the nanostructure. Gravity is a good example of the latter. It is a bulk force, which can be negligible in strength relative to surface interactions for nanoparticles. In one of his famous three 1905 papers, Einstein pointed out that gravity was unimportant for nanoparticles (referred to then as colloidal particles) in solution. He realized that in undergoing Brownian motion in a gravity field, such very small particles were essentially only subject to surface forces. As long as they did not agglomerate due to surface bonding as they bounced around while undergoing collisions, nanoparticles will stay in solution forever (Einstein 1905).

Smallness: surface versus bulk atom properties

The relative importance of surface versus bulk atoms and their properties influences the overall properties of nanograins and nanoparticles. The increasing surface atom to bulk atom number ratio that comes with decreasing size enhances the role of surface (boundary) atom spins, surface phonon scattering, surface electron scattering, and surface atom electric charge distribution (Fonash and Van de Voorde 2018).

An example of where this feature can be important can be found in the role of surface atom spins in ferromagnetic, ferrimagnetic, and antiferromagnetic materials. The bulk versions of these materials have magnetic domains, each of which has a magnetization, and each of which is defined by a boundary wall. These boundaries contain atoms whose spins carry out the transition from the magnetization of one domain to that of an adjacent domain. When such a magnetic material

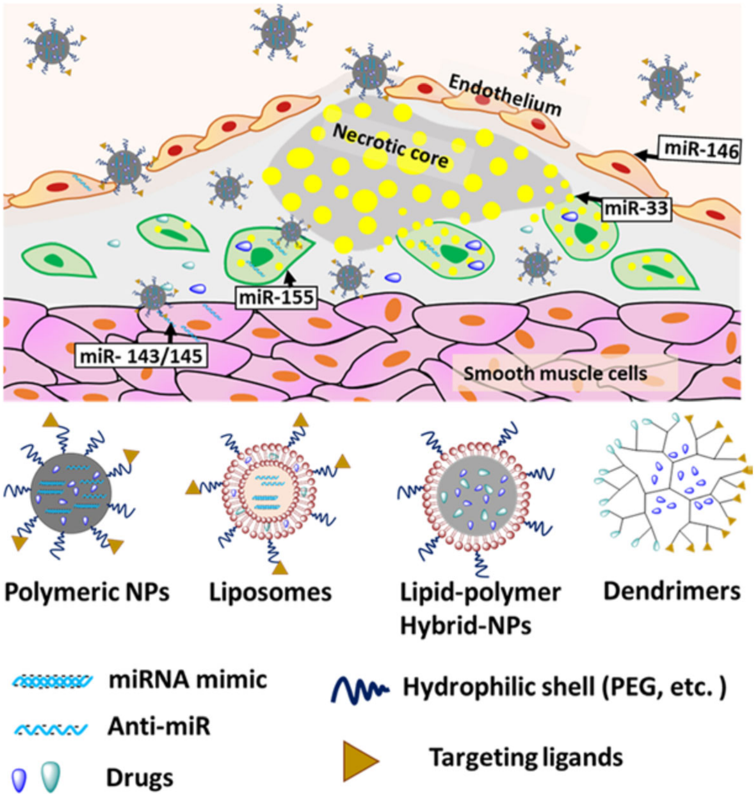

Fig. 1 Schematic representation of plaque on an artery wall. The plaque is being infiltrated by minute targeting nanoparticles such as those also shown. These nanoparticles can be functionalized by the example molecules sketched. The miR molecules depicted with black arrows in the plaque are microRNA precursors (reprinted with permission from Wolters Kluwer Health, Inc. (Gadde and Rayner 2016))

becomes of nano-size, a high fraction of the atoms will be involved in a domain wall (Mørup et al. 2010). As a consequence, in a nanoparticle or nanograin, the energy cost for forming the domain wall can become, with diminishing size, larger than the magnetostatic energy. In this case, it is energetically unfavorable to form domain walls and consequently the whole particle will be a single magnetic domain. The result is that nanoparticle or nanograin sizes of the order of, or smaller than a typical magnetic domain, will have a single magnetization. This magnetization is found to be parallel or antiparallel to what is termed “the easy axis,” an axis established by crystal structure or morphology (Mørup et al. 2010).

The “easy axis” magnetization in the nanoparticle will randomly flip back and forth under the influence of the nano-scale thermal fluctuations mentioned in Section 2 and discussed in Section 2.10. Consequently, for measuring times large compared to the flipping time, the magnetization of the nanoparticle or nanograin is, on the average, zero. This situation is very different from being in the ferromagnetic or ferrimagnetic state characteristic of the bulk material form. Since it is so different, the nanoparticle or nanograin, with this unique zero magnetization situation, is said to be in the superparamagnetic state. In this situation, the imposition of an external magnetic field is able to make one direction more energetically favorable thereby mitigating against the flipping, and consequently, uniformly magnetizing the nanoparticle or nanograin. The susceptibility for this response is quite high (Papaefthymiou 2009) resulting in the use of the preface “super” in the term characterizing this nano-scale phenomenon.

Superparamagnetic behavior found for some materials in the nano-scale is somewhat similar to the paramagnetic behavior of bulk materials. However, the magnetic susceptibility of those bulk materials is much smaller than that of the superparamagnetic nanoparticles. Because of their biocompatible size and this very large magnetic susceptibility, superparamagnetic nanoparticles can be used in medicine for magnetic resonance imaging (MRI). In this role, they function as contrast agents producing a strongly varying local magnetic field that enhances imaging (Gibby 2005).

Chemical bonding in nanostructures

Chemical bonding is obviously a nano-scale phenomenon itself. Interestingly, in some nano-scale structures, chemical bonding can be forced to adjust to the nano morphology resulting in unique versions. A very well-known demonstration of this phenomenon can be found in the single wall carbon nanotube (SWCNT) depicted in Fig. 2. The figure shows the single sheet of atoms of the SWCNT has features of the hexagonal bonding of carbon in graphite and graphene. However, unlike those materials, the bonding present in the SWCNT is contorted. The contortion (chirality) can have variable amounts of twisting depending on the process that produces a particular SWCNT (Fonash and Van de Voorde 2018). Other nano-scale structures have been found with such strained bonding configurations. For example, germanium is reported to form a buckled, strained-bond analogue of graphene (Acun et al. 2015).

Self-assembly

Conditions can arise at the nano-scale in which some combination of particles, atoms, or molecules can self-assemble itself into predetermined new materials and structures. Figure 3 gives an example. Here, an environment containing cadmium ions and the amino acid cysteine is utilized to produce CdS nanocrystals. These minute nanocrystals are then assembled by the non-photosynthetic bacterium *Moorella thermoacetica* onto its membrane by electrostatic interaction (a strong bulk force unlike gravity) (Fig. 3). Enzymes in the bacterium's membrane subsequently attach themselves to these nanocrystals resulting in a self-assembled photosensitive CdS-laden structure that, under illumination with photons having energies at or above the CdS band gap, can inject photogenerated electrons into the enzymes. This leads to electrons in the bacterium that can enhance CO_2 fixation thereby producing acetic acid. This self-assembly procedure results in the machinery seen in Fig. 3, in which the bacterium *M. thermoacetica* has turned itself into a photosynthetic structure capable of efficient CO_2 fixation (Sakimoto et al. 2016).

The bonding and morphology possibilities of DNA also can be used in self-assembly. In this case, rather than its serving as a carrier of biological information, DNA can be used to make complex 2D and 3D shapes. Such DNA structures have also been used as templates incorporating other molecules or nanoparticles into nanostructures (Fonash and Van de Voorde 2018). In general, self-assembly holds great promise for manufacturing approaches of the future which, in using self-assembly, could employ processing that is more in concert with nature.

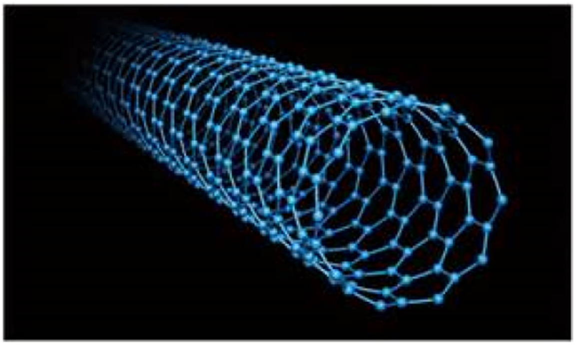

Fig. 2 The single wall carbon nanotube (SWCNT). Carbon atoms are represented by the spheres (reprinted with permission from Ananth Raman http://tinymatter.com 2014)

Quantum confinement and tunneling

The concepts of quantum mechanics such as quantization, quantum confinement, and tunneling are everyday

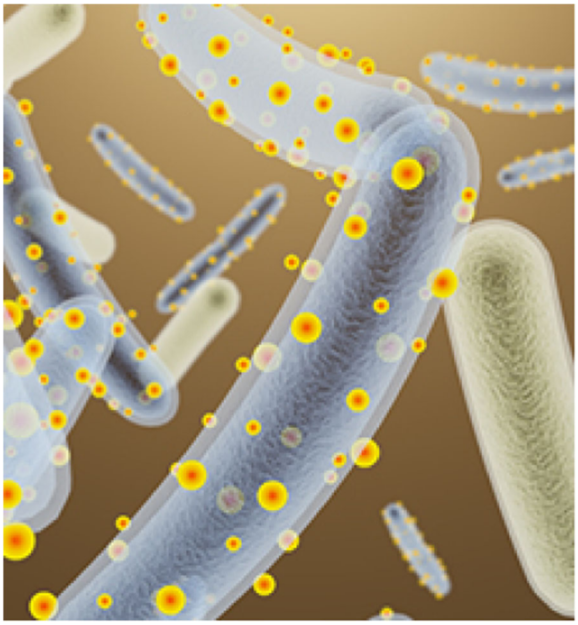

Fig. 3 The bacterium *Moorella thermoacetica* self-assembling itself into a photosynthetic structure capable of efficient CO_2 fixation (reprinted with permission from Sakimoto et al. 2016)

working ideas in nanotechnology. In the case of electron quantum confinement, the spatial restrictions of nano-scale structures can confine electrons resulting in the presence of energy levels whose values and spacing depend on the degree of confinement. Nano-scale structures can also display quantum tunneling, the opposite of confinement, in which an electron wave function leaks across classically forbidden energy barriers of nano-scale extent (Fonash and Van de Voorde 2018).

In the case of quantum confinement, the simple electron in a box "standard" quantum mechanics problem shows the link between spatial confinement and quantization of energy. Taking the solution for the situation of an electron in an infinitely deep 3D box and using that expression to give the difference $[E_{(n+1)} - E_n]$ between two energetically adjacent electron energy levels gives (Fonash and Van de Voorde 2018):

$$E_{n+1} - E_n = \frac{h^2}{8m_e L^2}[2n+1] \tag{1}$$

Here, h is Planck's constant, m_e is the electron mass, and Lx L x L defines the confining volume. This simple statement in (1) shows confinement can influence the energy values allowed and their spacing. It also shows decreasing L increases the inter-level spacing.

To look more closely at the role of scale, we use Eq. 1 to form the ratio of adjacent energy level differences, one difference for the micro-scale, and the other is for the nano-scale. The result is

$$\frac{[E_{n+1} - E_n]_{\text{Micro}}}{[E_{n+1} - E_n]_{\text{Nano}}} = \left[\frac{L_{\text{Nano}}}{L_{\text{Micro}}}\right]^2 \tag{2}$$

with $[E_{n+1} - E_n]_{\text{Micro}}$ for the micro-scale and $[E_{n+1} - E_n]_{\text{Nano}}$ for the nano-scale. Taking the ratio $\frac{L_{\text{Micro}}}{L\text{Nano}}$ to be 10^{+3} shows the two corresponding adjacent energy levels are 10^6 times farther apart in energy for the nano-scale than they are for the micro-scale. In other words, quantization of energy can be quite discernable at the nano-scale due to confinement. However, for micro- and larger scales, this quantization is not easily observed and energy can appear as a continuum of values. The dependence of the fluorescence wavelength on quantum dot (QD) size is an example of quantum confinement in nanoparticles.

Wave-particle duality

The wave-particle duality of quantum mechanics can be quite evident in confined nano-scale structures. For example, tunneling is described in terms of a particle's wave function leaking out of a confining region. In scattering situations, modulation patterns can be set up that reflect quantum interference between particle waves that are scattered off the boundaries of a nanostructure thereby forming a standing wave (Oka et al. 2010).

Figure 4 gives a well-known example showing the interference of particle wave functions (Crommie et al. 1993). This figure shows a standing wave which is producing the experimentally determined probability density seen in Fig. 4. This probability gives the location of electrons trapped in a "corral" of atoms sitting on a surface. The corral atoms have been dragged into this configuration with a nano-scale probe. Valence electrons from these dragged atoms have gone into the corral and their resulting experimentally determined position-probability distribution produced by their wave functions is seen. The image in Fig. 4 is created by electron wave function leakage (tunneling) induced out of the electron distribution positions predicted by the wave interference pattern. This leakage is caused in this case by using a scanning nano-scale probe biased positively with respect to the surface.

Relativistic phenomena at the nano-scale

Amazingly, relativistic behavior can emerge for fermions in some nano-scale situations (Fonash and Van de Voorde 2018). When present for electrons, the telltale signature is seen in a material's electron E-k dispersion.

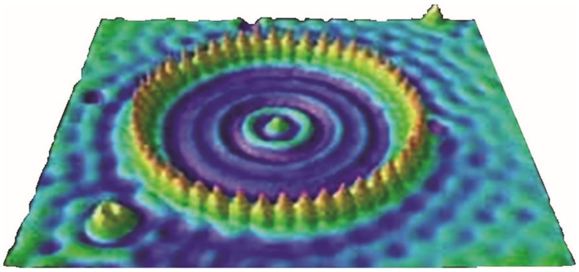

Fig. 4 Atoms arranged on a surface to form a corral confining their valence electrons. The probability density image—determined by the wave function distribution—has been captured by scanning tunneling microscopy, i.e., by wave function leakage into a positively biased scanning probe (reprinted with permission from AAAS (Crommie et al. 1993))

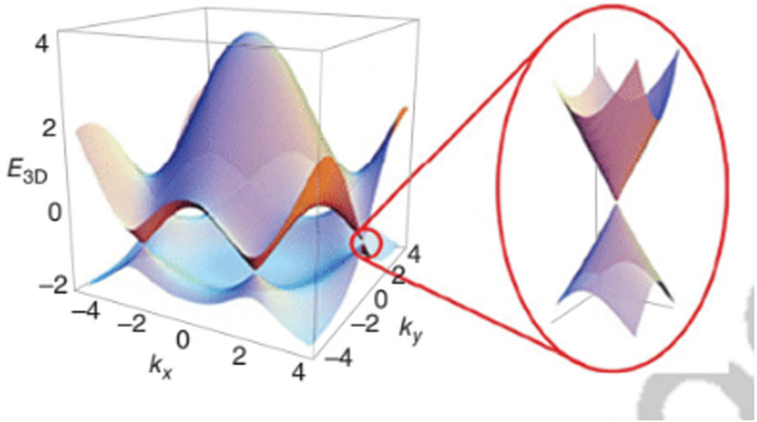

Fig. 5 Electron dispersion relation for graphene. Linear dependence of electron energy *E* and, consequently, the resulting Dirac cones are seen at symmetry points of the 2D *k*-space (from Castro Neto et al. (2009), with permission from American Physical Society)

Specifically, the E-k relation will exhibit a linear region in k-space which is home to the mass-less Dirac electrons (Wang et al. 2015; Castro Neto et al. 2009). Figure 5 shows an example of this linear E-k behavior as it appears for the 2D material graphene. Since graphene's Brillouin zone is also 2D, its dispersion relation manifests its linearity in what are termed the Dirac cones in Fig. 5. Interestingly, we note that a very different particle in nature, the photon, can display a linear dispersion relationship and mass-less features. A set of materials with these mass-less Dirac electrons are topological insulators (TIs). These materials may also harbor Majorana fermions. These are proposed particles which interestingly, if present, would be their own anti-particles (Fonash and Van de Voorde 2018).

The appearance of Dirac cones for some nano-materials signals that relativistic/quantum phenomena can be important, and therefore, the Dirac relativistic/quantum mechanical formalism should be used to describe electrons in such a material (Fonash and Van de Voorde 2018). Mass-less behavior can produce very unusual properties including ballistic (collision-free) charge transport, unusual Hall effects, enormously high carrier mobilities, and topologically dependent phases (Zhang et al. 2015).

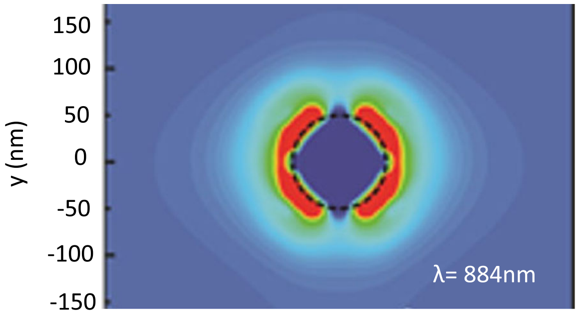

Fig. 6 Computer solution of Maxwell's equations to obtain the light intensity in and around a Ag nanoparticle produced by a plane wave (wavelength 884 nm) impinging from large y onto the particle. Surface plasmon excitation at the Ag nanoparticle periphery is seen, as is the near-field region

Electromagnetic interactions with nanostructures

Unique material-electromagnetic field interactions can occur at the nano-scale. These can involve both quantum as well as E-M wave effects. Figure 6 shows such a situation. Here, what is termed the plasmonic mode of a metal nanoparticle has been excited by the electric field of an incoming light wave. This mode is a cooperative excitation of the essentially free, valence electrons of a metal nanoparticle. The electrons in the nanoparticle in this mode are all following, in unison, the impinging electric field requiring that the wavelength λ of the incoming light must be large compared to the size of the nanoparticle. This plasmon excitation, as a quantum of this oscillating electron motion is called, can relax resulting in the reradiation of photons from the nanoparticle. In addition, energy can also be lost due to collisions of these oscillating valence electrons within the particle. The electric field distribution caused by the plasmon excitations of the metal nanoparticle has a radiating far-field component corresponding to the emitted photons and a strong near-field component around the nanoparticle. This high field is seen to fall off in Fig. 6 with a characteristic length of the order of the nanoparticle size.

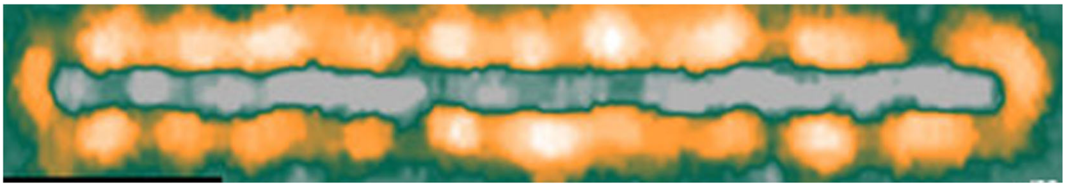

Fig. 7 A 3.4-μm-long, ≃ 45-nm radius isolated Ag nanowire with a photoinduced SPP standing wave (reprinted with permission from Springer Nature (Piazza et al. 2015))

Electromagnetic radiation can also be converted to localized electromagnetic energy in situations for which there is an interface between a metal and a dielectric. This localized energy is termed a surface plasmon polariton (SPP). The SPP particle is the coupling between the plasmon at the metal surface and the polariton, the evanescent, radiated electromagnetic field confined in the direction perpendicular to the interface (Fonash and Van de Voorde 2018).

The wave aspect of SSPs has been established (Piazza et al. 2015). SPPs have been found to be able to form standing waves as seen in the experimentally imaged, SPP standing wave in the Ag nanowire of Fig. 7. While SPPs are bound to the metal surface in the perpendicular direction, they can propagate non-radiatively along the surface, and as such can be guided relatively unperturbed through bends, corners, or virtually any arbitrary

Table 1 The 10 unique features of the nano-scale

Feature	Cause	Example of Impact
Smallness: physical size	Size of nanoparticles; nanograins	Medical targeting for therapy and imaging
Smallness: surface versus bulk forces	Surface to volume ratio	Nano-scale materials can melt at temperatures as much as hundreds of degrees lower than their bulk counterparts.
Smallness: surface versus bulk atom properties	Surface to volume ratio	Use of nanocrystalline materials to improve strength
Chemical bonding possibilities in nanostructures	Size and morphology	Graphene is the strongest reported material.
Self-assembly	Enabled by bonding and morphology	DNA self-assembly is used to make complex 2D and 3D structures with both tile-based and DNA origami-based approaches.
Quantum confinement; tunneling	Sizes that can control allowed energy levels and particle wave locations	Variable color capabilities from QDs
Wave-particle duality	Can be observable since particle waves can be the size of nanostructures	Basis of tunneling microscopy
Relativistic behavior	The structure and nano-thickness of 2D materials can result in presence of Dirac electrons.	Can produce very high semiconductor electron mobilities
E-M waves and nanostructure interactions	E-M waves interacting with, nano-features	Plasmonics
Thermal and quantum fluctuations	Thermal fluctuations: nano-systems may not have the requisite huge numbers needed for statistics causing observable statistical fluctuations around the average Quantum fluctuations: $\Delta E\ \Delta t \geq \hbar$ coming into play in small regions	Thermal fluctuations: 2nd law becomes increasingly blurred and statistical fluctuations around the average become more observable Quantum fluctuations: result in the Casimir "force" thereby affecting friction and striction

metallic nanostructure (Piazza et al. 2015). In addition, the quantized particle nature of SPPs has been shown to be the same as that of the photon of a free space electromagnetic field.

Fluctuations

Because sizes are so small at the nano-scale, nanotechnology systems can display the extremely unique phenomena of thermodynamic fluctuations and of quantum fluctuations (Fonash and Van de Voorde 2018). These fluctuations can make the data from experiments in nano-scale systems, such as biological molecular motors and nano-scale magnets, messy and difficult to understand.

Discussing thermal fluctuations first, we note that their origin lies in the fact that as a system gets succeedingly smaller, fluctuations away from the thermodynamic equilibrium distribution begin to become important (Fonash and Van de Voorde 2018). This is not surprising, since the thermal properties present at thermodynamic equilibrium emerge from the statistics of huge numbers and nano-systems may not have the requisite huge numbers (Jarzynski 2011). Jarzynski has suggested that one way to consider thermal fluctuations in nano-systems is to envision the familiar standby of thermodynamics, the gas-and-piston setup. In this picture, a first setup contains a gas which begins in a state of thermal equilibrium inside this container with its adiabatic walls (Jarzynski 2011). If the piston is rapidly pushed into the gas in the macro-scale version and then pulled back to its initial location, there will be a net increase in the internal energy of the gas. However, in a nano-scale version of this setup, an increase in the internal energy is not mandated with the piston motion. That is, for a gas with only a few particles, we could observe—rarely perhaps—a decrease in internal energy depending on how the small number of particles is moving (Jarzynski 2011). However, on the average, we still expect an increase in the internal energy to hold.

This type of behavior could be dismissed as uninteresting noise that merely reflects poor statistics due to a small N. Importantly, the example actually suggests the following perspective: as we apply the tools of thermodynamics to ever-smaller systems, the second law becomes increasingly blurred and statistical fluctuations around the average become ever more observable and ever more important as fewer particles are in play (Jarzynski 2011).

The other types of fluctuations of importance at the nano-scale, quantum fluctuations, have no link to statistics nor to thermodynamics. In addition, although quantum fluctuations can be very important at the nano size range, they are not due to smallness itself but to the small separation distances that can be present between objects at the nano-scale (Fonash and Van de Voorde 2018). Basically, quantum fluctuations arise from the temporary change ΔE in the amount of energy (or, importantly, mass or particles, since they are equivalent) that can occur in a region for a time Δt, the fluctuation time. Consequently, conservation of energy is violated during the fluctuation time. All of this follows from Heisenberg's Uncertainty Principle (Eq. 3) which relates these two quantities ΔE and Δt (Fonash and Van de Voorde 2018):

$$\Delta E\,\Delta t \geq \hbar \qquad (3)$$

Quantum fluctuations can be important specifically at the nano-scale because the number of particles created in Δt, within a nano-separation, can be much smaller than the number created outside that region due to the spatial compatibility of the waves of all these particle (Capasso et al. 2007). This creates a "pressure" that tries to push objects having a nano-scale separation together thereby giving rise to what is termed Casimir "force." The result for nano-scale separations is that the Casimir force can affect friction and even result in striction (the permanent adhesion of surfaces). The Casimir force can be a very critical problem for moving systems at the nano-scale since this "force" increases with decreasing spacing (Capasso et al. 2007).

Summary

This article has presented a listing of 10 unique features of the nano-scale size range. These are summarized in Table 1. They are responsible for making the field very broad, interesting, and impactful. They also are responsible for making this size scale quite rich in opportunities for new products, new materials, new methods, and new structures.

Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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